

HYDROPROCESSING OF DESALTED DIRECTLY LIQUEFIED BIOMASS

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ABSTRACT

Desalted directly liquefied biomass from the PERC process was consecutively extracted with iso-octane and xylene. The hydroprocessing was made in a downflow reactor at a constant hydrogen flow and pressure of 85 normal l/h and 10.0 MPa, respectively. The catalyst used was a sulphided cobalt + molybdenum catalyst on gamma alumina. At a liquid flow of 180 ml/h, an hourly liquid space velocity of 1.20 and a temperature of 350°C, the oxygen content of the desalted oil was reduced from 15.3 to 2.3 percent by weight. The effective H/C molar ratio was increased from 1.05 in the starting material to 1.35 and the amount of heavy material with normal atmospheric boiling points above 540°C was reduced from 45.3 to 15.1 percent by weight. Hydroprocessing at 420°C reduced this heavy material further to 4.5 percent by weight. The deoxygenation was only to a small degree dependent on whether the feed oil was desalted or extracted with iso-octane or xylene.

INTRODUCTION

Hydroprocessing is the most important method to reduce the amount of heteroatoms. Oil produced from biomass contains high amounts of oxygen. Downflow trickle bed reactors are the major type used in hydroprocessing of gas oil and heavier types of petroleum fractions. By using similar systems when upgrading oil produced from biomass, known techniques can be used, thereby achieving lower costs. Furthermore, existing refineries can be used without major rebuilding. Elliott and Baker (1-3) have carried out several experiments in an upflow hydroprocessing reactor. When using a downflow reactor they got severe coking and plugging of the flow. They also claim that at low hold up times, which they used, upflow reactors are better than downflow (1).

Petroleum contains small amounts of inorganic salts, mainly sodium chloride. The inorganic salts will be deposited on heat exchange surfaces and on catalysts in distillation towers. By desalting, the inorganic salts are washed out of the oil. The oil used in this study contains approximately 1% of sodium which is considerably more than what is found in petroleum (4).

Earlier work in our laboratory (5) was based upon the assumption that the crudest part has to be separated out before sensitive hydroprocessing catalysts can be used. Since the oil is more thermally instable than petroleum, extraction has been the method employed. By selecting certain solvents it is possible to receive a predicted yield. However, when separating out the residual part of the oil, large losses occur and the overall yield will be low (4). Therefore, it is of interest to establish a minimum level of amount of residue at which extraction should be performed, without negative effects in the hydroprocessing step.

The purpose of this study was to find a level for suitable yields in the extraction step and still have good conversions without severe deactivation in the hydroprocessing step. Since desalting was included the oil before extraction can also be hydroprocessed. Another important objective was to employ a downflow hydroprocessing reactor. In this paper some preliminary results are presented.

EXPERIMENTAL

Feed oils

The feed oil used was produced from Douglas Fir by the PERC Process in test run 13, in the Albany Liquefaction Plant (6). The oil was mixed with 10 percent by weight of iso-octane, desalted with water at 95°C at a ratio of 1 part oil to 2 parts of water (by volume). It was settled overnight and the desalting was repeated once (referred to as oil D). The sodium content of the feed oil was in this way reduced from 0.92 percent by weight to 0.12 percent. Oil D was consecutively extracted with iso-octane and xylene. The solvents were stripped from the extract in a thin film distillation unit (KDL4 Leybold Heraeus). The two oils will be referred to as oil O and oil X respectively. The residue from the extraction was not treated further. Carbon disulphide was added to the feed oils before hydroprocessing to approximately 100 ppm by weight. The reason for this was to maintain a constant activity and selectivity of the sulphided catalyst (2, 7).

Catalyst

The catalyst used was CoMo on gamma alumina containing 4.2 % CoO and 15.0 % MoO₃ (Akzo Ketjen 742). Prior to use, the catalyst was sulphided with a mixture of 13% hydrogen sulphide in hydrogen at 315°C, 0.3 MPa total pressure and 7 hours of reaction time. In each run 150 ml of catalyst was diluted with 50 ml of carborundum.

Reactor system

The reactor system was a continuous downflow trickle bed designed by Cities Service and modified for heavy feed stocks. The oil was preheated in the feed tank and further heated in the fluidized sandbath before entering the reactor. The liquid product was stripped after reaction (Figure 1).

Analysis

Carbon and hydrogen were determined with a LECO CHN-600 instrument. Oxygen and sulphur were determined with a LECO RO-116 and a LECO SC-132 respectively. Material balance of the liquid products were calculated based on determinations on GC (HP 5880) and GPC according to procedure in reference 4. Coke on catalyst was measured after sohxlet extraction with xylene for 24 hrs. and vacuum drying for 24 hrs. at 110°C. A blank value of 2.04% was reduced from the measurement.

RESULTS AND DISCUSSION

Results of feed stock characterization

Oil O has a higher H/C ratio and a lower oxygen content than the other oils, see Table 1. The fraction of oil O boiling above 540°C is also considerably lower. Thus oil O has good characteristics for being upgraded. Oil D has a higher oxygen content and a poorer H/C ratio than the other two oils. Finally, oil X has the same low H/C ratio as oil D but a considerably lower oxygen content, 9.5 versus 15.5 for oil D.

Results of hydroprocessing

Hydroprocessing of the three oils under similar conditions improved the H/C ratio of all oils but, surprisingly, most in oil D (Tables 1 and 2). Oil O seems to be less active than the other two oils in the HDO reactions since the oxygen content is reduced from 8.2 to 4.8 percent while the reduction of oxygen is higher in the other two oils. The experiments also show that oil O is not cracked to the same degree as the other two oils (Table 3). In biomass the cellulose is built by connecting glucose molecules through C - O - C linkages. Furthermore, lignine is connected with C - O - C bindings although less frequently than in cellulose. A material of the liquefied biomass with large molecules is likely to have large amounts of C - O - C bindings remaining. The C - O - C bindings are easier to break than

C - C bindings in hydroprocessing. This might explain the higher reduction of oxygen and molecular sizes of oil D than that of the other two oils. The residue from the extraction of the feed oil was not further tested since the viscosity was too high. By comparing the cracking and deoxygenation of oil O, X and D and the fact that oil O, X and the residue from extraction together forms oil D. The residue must show a higher activity for cracking and deoxygenation than oil O, X and D. However, on the other hand there might be components in oil O and X which are necessary for deoxygenation and cracking of the residue from extraction.

The largest surface area of the catalyst is found in pores with a diameter between 25 - 80 Å. For a complete pore distribution of the catalyst used, see reference 8. Larger molecules will be limited by diffusion and even not able to enter the smallest pores. The conversion of the largest molecules (C_{44+}) is a strong indication that thermal reactions or homogenous catalysis is important (Table 3). When hydroprocessing in another system, Gevert and Otterstedt (8) showed high conversions without any catalyst present.

Coke on catalyst was measured after the runs and showed high amounts in all cases (Table 4). The high amounts of coke on the catalyst from the experiment with oil O cannot be explained with the limited amounts of experiments in this preliminary study.

In a special run (No. 1) with oil D, a higher temperature, 420°C, was used instead of 350°C (Table 1 and 2). The higher temperature gave considerably more coke on catalyst, 24%, as compared to 11% for the lower temperature (run No. 2). The conversion of heavier material (C_{44+}) was also much higher which has also been found earlier.

CONCLUSIONS

Downflow hydroprocessing of desalted oil from biomass has been successfully done. The preliminary experiments indicate that the residue after extraction with iso-octane and xylene has a higher activity in hydro-deoxygenation and cracking than the extracted oils. Extraction before hydroprocessing is not necessary.

ACKNOWLEDGEMENT

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LITERATURE CITED

1. Elliott, D.K., Baker, E.G. Biotechnology and bioengineering Symposium. 1984, No. 14, 159-174.
2. Elliott, D.C., Baker, E.G. in Proceedings of the 17th Biomass Thermochemical Conversion Contractors Meeting, 1985, CONF-8510167, NTIS 1985.
3. Baker, G.B., Elliott, D.C. Preprint paper - American Chemical Society, Div. Fuel Chemistry. 1987, 32, No. 2, 257-263.
4. Gevert, S.B. Refining of directly liquefied biomass to transportation fuels, IGT Conference on Energy from Biomass and Wastes X, Orlando, March 16-20, 1987.
5. Gevert, S.B., Otterstedt, J-E. Upgrading of liquefied biomass to transportation fuels by extraction. IGT Conference on Energy from Biomass and Wastes X, Washington D.C., April 7-10 1986.
6. Thigpen, P.G., Berry, W.L. In reprints IGT Conference on Energy from Biomass and Wastes VI, Lake Buena Vista, Florida, January 25-29 1982. pp. 1057-1095.

7. Gevert, S.B., Otterstedt, J-E., Massoth, F.E. Applied Catalysis, 1987, 31, 119-131.
8. Gevert, S.B., Otterstedt, J-E. Biomass, 13, 1987, 105-115.

Table 1 Experimental conditions in the different runs

Run No.	1	2	3	4
Oil	D	D	X	O
Temperature (°C)	420	350	350	350
Oil flow (ml/h)	170	180	170	110
LHSV	1.7	1.2	1.13	0.79
Experimental time (h)	6	6	6	6

Table 2 Elemental composition (in weight percent) of the different oils before and after experiments

Oil/Element	C	H	O	H/C*
D	70.6	8.2	15.5**	1.00
X	81.0	8.2	9.5	1.04
O	80.6	9.4	8.2	1.29
1	76.8	10.2	3.1	1.53
2	85.9	10.4	2.3	1.41
3	86.5	9.8	2.5	1.32
4	84.3	9.8	4.8	1.31

*The hydrogen to carbon ratio has been calculated under the assumption that the present oxygen consumes the hydrogen.

**Part of this 15.5 % of oxygen is due to organic oxygen in the oil, some remaining salts and also partly due to oxygen in the water.

Table 3 Boiling point characteristics of the oils in weight percent (values have been normalized)

Oil/Interval	-C ₄	C ₄ -C ₁₂	C ₁₃ -C ₂₀	C ₂₁ -C ₄₄	C ₄₄ +
D	0	1.7	25.0	42.1	31.2
X	0	2.9	31.6	44.7	20.8
O	0	5.0	49.3	42.8	2.9
1	0	18.0	43.1	34.6	4.3
2	0.1	20.0	36.5	29.8	13.6
3	0.2	17.9	37.7	29.7	14.5
4	0	13.3	45.9	33.5	7.32

Table 4 Coke on catalyst in weight percent and hydrogen consumption in vol. hydrogen/vol. oil.

No.	Coke	Hydrogen consumption
1	24.0	-
2	11.0	-
3	11.1	152
4	21.4	81

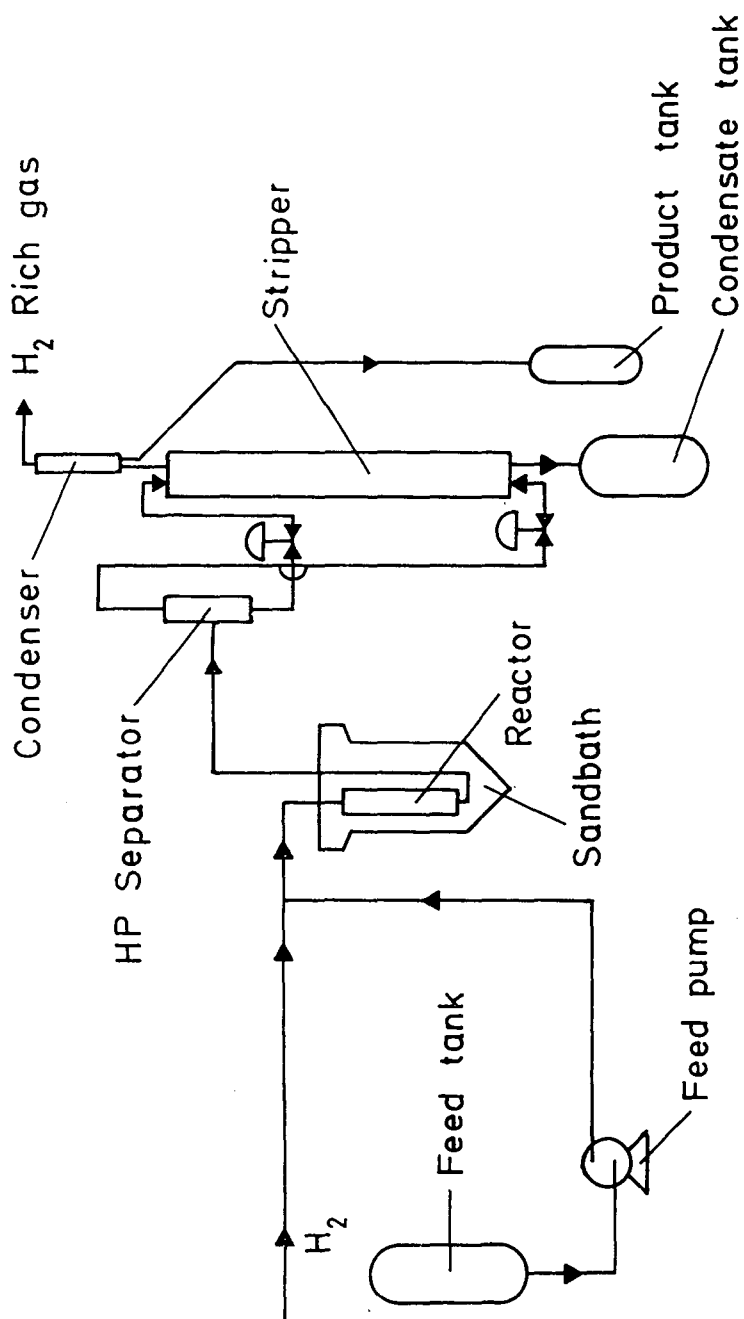


Fig.1 Principle flow diagram of hydroprocessing equipment.